**CLAIMS:**

1. A method of analyzing a substance, the method consisting of:

(1) creating a stream of ions in said substance;

(2) supplying the stream of ions and a collision gas to a multipole and providing an RF signal to the multipole, whereby the quadrupole functions as a collision cell;

(3) fragmenting said ions in the RF multipole by collisions with the gas molecules, in order to form primary fragment ions;

(4) supplying additional alternating current to the multipole at a frequency selected to cause resonance excitation of a desired primary fragment ion mass-to-charge ratio, whereby ions with said desired primary fragment ion mass to charge ratio are excited and undergo collisions with the gas molecules causing production of secondary fragment ions;

(5) modulating the alternating current signal applied in step (4) whereby periods in which said alternating current signal is applied alternate with periods in which the alternating signal is not applied;

(6) detecting the ion signal after fragmentation with a mass spectrometer and collecting one set of data for one spectrum, representative of the ion spectrum when the alternating current signal is applied and another set of data for another spectrum, representative of the ion spectrum when the alternating current signal is not applied;

whereby said other spectrum can be subtracted from said one spectrum, to generate a subtracted spectrum showing the secondary fragment ions without the presence of the primary fragment ions except for any said primary fragment ions which are generated by step (4), whereby to obtain $MS^3$ information.

2. A method as claimed in claim 1, further including the step of processing the data sets by applying statistical analysis to reject spectra having statistically insignificant variations in the ion signal.

3. The method as claimed in claim 2, wherein the statistical analysis is implemented in a software program and performed automatically.

4. The method as claimed in claim 3, wherein the statistical analysis is performed in real time so that spectra having statistically insignificant variations in the ion signal are not displayed.

5. A method as claimed in claim 1, wherein, said multipole is a quadrupole.

6. A method as claimed in claim 5, which includes applying the alternating current signal at a frequency that excites the desired primary fragment ion.

7. A method as claimed in claim 5, which includes passing the stream of ions through a first mass analyzer to select a precursor ion mass to charge ratio of interest, and passing the precursor ions into the collision cell.

8. A method as claimed in claim 7, which includes providing a potential difference between the first mass analyzer and the collision cell, to accelerate the precursor ions into the collision cell, whereby the precursor ions gain sufficient velocity to collide with the collision gas to cause fragmentation, and wherein step (4) comprises applying an alternating current signal to excite the desired primary fragment ions.

9. A method as claimed in claim 7 or 8, which includes applying a second alternating current signal to the quadrupole rod set, to excite the secondary fragment ions generated in step (4), thereby to generate tertiary fragment ions and wherein step (5) comprises modulating the second

alternating current signal.

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10. A method as claimed in claim 1, 2, 3, 4, 8 or 9, which includes subtracting said one spectrum from the other spectrum to obtain a subtracted spectrum.

11. A method as claimed in claim 9, which includes subtracting said one spectrum from said other spectrum to obtain a subtracted spectrum.

12. A method as claimed in claim 10, which includes, for each peak, recording a plurality of data points encompassing the peak, and calculating a significance factor equation:

$$|T| = Sig = \left| \frac{\text{detected ion signal, alternating current on} - \text{detected ion signal, alternating current off}}{\sqrt{\sigma^2\text{alternating current on} + \sigma^2\text{alternating current off}}} \right|$$

and determining from the values of $|T|$ of the ion signal whether the detected ion signal with alternating current on created ions that significantly contributed to said peak.

13. A method as claimed in claim 7 or 8, which includes applying a plurality of steps of selecting a desired fragmentation and applying an alternating current signal to generate additional fragment ions, wherein step (5) comprises modulating the last applied alternating current signal, whereby in step (6) said one spectrum includes said additional fragment ions formed by said last applied alternating current signal and said other spectrum comprises ions generated without application of said last applied alternating current signal.

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14. An apparatus, for analyzing a substance by resonance excitation of selected ions and selective collision-induced dissociation, the apparatus comprising:

an ion source for generating a stream of ions;

a collision cell, including a quadrupole ion guide, for receiving a stream of precursor ions and provided with a collision gas, for collision-induced dissociation between the parent ions and the buffer gas;

a power supply connected to the quadrupole rod set for generating an RF field in the quadrupole rod set for guiding ions and for applying an additional alternating current field at a frequency selected to excite a desired ion;

a modulation means connected to the power supply, for modulating the alternating current signal, whereby periods in which said alternating current signal are applied alternate with periods in which the alternating current signal is not applied.

15. An apparatus as claimed in claim 14, which additionally includes a detector for detecting fragment ions exiting the collision cell, a switch connected to the detector, two data storage devices connected to the switch, and a connection between the modulation control unit and the switch, whereby the switch switches detected data for periods when the alternating current signal is applied to one data storage device and collected data for periods when the alternating current signal is not applied to the other storage device.

16. An apparatus as claimed in claim 14, which includes a second power supply connected to the quadrupole rod set, a second modulation unit connected to the second power supply and also to the switch, before applying a second alternating current signal, for excitation of a second ion.

17. An apparatus as claimed in claim 15, which includes a first mass analysis section for selecting a parent ion.

18. An apparatus as claimed in claim 16, which includes a final mass analysis section, including the detector, for analyzing fragment ions

from the collision cell.

19. An apparatus as claimed in claim 17, wherein the final mass analysis section comprises one of:

a scanning mass analyzer and a detector; and

a time-of-flight device, including the detector for providing a small spectrum.